Nutritional properties of fruits and vegetables

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CHAPTER

5 Nutritional Quality of Fruits and Vegetables

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Introduction

Chronic diseases such as heart disease, stroke, cancer and diabetes are a leading cause of mortality worldwide. Excess weight and outright obesity are a growing concern. Prevention of these problems is linked to lifestyle choices. There may be an evolutionary discordance between modern diets, rich in calories from fats and starches and low in fruits and vegetables, and human nutritional requirements (Martin et al., 2013). Consequently replacing some added sugars and saturated fat with more fruits and vegetables may benefit health**.** A growing body of research indicates that fruit and vegetable consumption reduces the risk of major diseases and possibly delays the onset of age-related disorders. Traditional eating patterns of the Mediterranean region are associated with reduced cardiovascular disease. Although there is no single definition of a Mediterranean diet, descriptions emphasize the consumption of vegetables, fruits and nuts (USDA, 2010).

The dietary constituents obtained from fruits and vegetables include water, fiber, proteins (more abundant in legumes), sometimes fats (olive, avocado, nuts), organic acids and digestible carbohydrates. Starch-based staples (potato, cassava, corn, banana, plantain) provide a major energy source in some regions. Fruits and vegetables provide minerals and vitamins. They are the main dietary source of vitamin C and a significant source of pro-vitamin A and vitamin B_6. Compared to other food sources, they are high in potassium and low in sodium. Ascorbic acid in fruits and vegetables may enhance the bio-availability of dietary iron. Fruits and vegetables provide unique and appealing textures, colors and flavor, they are relatively low in calories (excluding staple crops) and are cholesterol-free. They also include a variety of non-nutritive bioactive phytochemicals with health

Postharvest Handling.

benefits. Some constituents of horticultural crops that help to prevent disease include fiber, phytosterols, carotenoids such as lycopene, ascorbic acid, tocopherols, glucosinolates, thiosulfinates and phenolics such as flavonoids, hydroxycinnamic acid-derivatives, stilbenes and catechins (Voutilainen et al., 2006; Ignarro et al., 2007; Holst and Williamson, 2008; Chen and Chen, 2013). Fruit phytochemicals and diet constituents may exert antagonistic, additive or synergistic effects (Heinonen et al., 1998). Although the mechanisms by which fruits and vegetables promote human health are unclear, current evidence has led to recommendations that healthful diets include a variety of fresh or processed horticultural commodities (www.dietaryguidelines.gov). In spite of these guidelines, fruit and vegetable intake is often below the dietary goal of five to 10 servings or 400 g of fruits and vegetables daily. Less than a quarter of the total population reaches the recommended intake of fruits and vegetables in America and European Union countries (Martin et al., 2013).

Fruits and vegetables may be incorporated in different raw or cooked, fresh or processed forms: canned, pickled, dried, frozen, candied, and in sauces, purees or preserves. Juices are good sources of phytochemicals and vitamins and can also contribute to the overall fruit and vegetable intake. However, they contain less fiber than unprocessed commodities and may contribute extra calories if sugar is added. Care must be taken regarding added salt in processed vegetable products, since they may contribute up to one-third of the total dietary sodium intake (Hiza and Bente, 2007).

In this chapter, we describe the main nutritional components and non-nutritional antioxidants present in fruits and vegetables, with special reference to the latest advancements. The influence of species, cultivar, maturity stage and postharvest storage conditions on these components is discussed.

II Nutrient components

A Water

Water comprises ~60% of the body's weight and is essential for good health. An intake of 2.2 or 3.0 l of total beverages a day is recommended for men and women. Individual needs depend on environmental conditions, diet and physical activity. Water is also the most abundant single component of fresh fruits and vegetables and in leafy vegetables it may be up to 95% of the mass. The percentage of water varies among individual fruits and vegetables due to structural differences and the developmental stage.

B Proteins and nitrogen compounds

Proteins represent <1% of the fresh mass of most fruit and vegetable tissues. Legumes may contain 15 to 30% protein. Nuts and sprouts are also good sources of high quality proteins. Vegetables and legumes account for ~6.0% of protein intake in the United States, while fruits only contribute 1% (Hiza and Bente, 2007).

Some plant seeds, particularly legumes, contain some anti-nutritional proteins. Soybean trypsin inhibitors have been a concern since they can reduce protein utilization. However, common processing methods such as cooking may inactivate the protease inhibitory activity (Lajolo and Genovese, 2002).

A number of non-protein nitrogenous compounds including free amino acids, chlorophylls, polyamines or alkaloids are also present in fruits and vegetables. In potatoes, 50–60% of the nitrogen occurs either as free amino acids or in other non-protein metabolites, while in apples estimates range from 10 to 70% (Salunkhe et al., 1991). Senescent tissues and overripe fruits may contain greater proportions of non-protein nitrogen. Asparagine is abundant in potatoes and apples. Pears and oranges are rich in proline and black and red currants in alanine.

The nitrogen steroidal glycoalkaloids (GLS) α-solanine and α-chaconine are acetylcholine esterase inhibitors found in potato tubers which can induce neurological disorders. Solanin is present at the highest concentration immediately under the skin and usually makes up ~8 mg/100 g fresh weight (FW). Concentrations exceeding 20 mg/100 g FW are considered unsafe for human consumption (Itkin et al., 2013).

C Lipids and fatty acids

Lipids may be used as energy sources and are the main components of cellular membranes and waxes. They are mainly present as triglycerides (esters of glycerol and three fatty acids). However, diverse chemical forms co-exist within this group. Phospholipids, in which one fatty acid is replaced by phosphoric acid, are also important membrane constituents. The fat concentration varies with the commodity, but most fruits and vegetables have <1% lipid, with avocadoes, olives and nuts being the exceptions. Fats comprise 35–70% of dry mass in the avocado and olive, but only 0.2% of grape, 0.1% of banana and 0.06% of apple.

The physical and chemical properties of lipids are largely determined by their constituent fatty acids. Fatty acids in foods are usually aliphatic and monocarboxylic. They may be saturated or unsaturated to varying degrees and may contain from four to 26 carbons. Oleic (18:1) and linoleic (18:2) acids are the most prevalent. Olive oil and other fats high in monounsaturated fatty acids can help lower low-density lipoprotein (LDL)-cholesterol (so-called "bad" cholesterol), while protecting high-density lipoprotein (HDL)-cholesterol ("good" cholesterol) when consumed in moderation in place of saturated fats. Fats derived from animal sources (e.g., butter, cream, hard cheeses) have a high proportion of saturated fats, while oils from plant sources such as olive and canola have the lowest (Table 5.1).

Fatty acids are required for human body functions as they are used to produce lipids and hormone-like substances that regulate blood pressure, blood clotting and immune and inflammatory responses. The human body can produce most fatty acids except linoleic acid and α-linolenic acids, which are common in plant

Table 5.1 Fatty Acid, Vitamin E, and Cholesterol Composition of Some Common Dietary Fats

	Saturated (%)	Monounsaturated (%)	Polyunsaturated (%)	Cholesterol (mg/100 g)
Animal fats				
Lard	40.8	43.8	9.6	93
Butter	54.0	19.8	2.6	230
Vegetable fats				
Coconut oil	85.2	6.6	1.7	0
Palm oil	45.3	41.6	8.3	0
Cottonseed oil	25.5	21.3	48.1	0
Wheat germ oil	18.8	15.9	60.7	0
Soya oil	14.5	23.2	56.5	0
Olive oil	14.0	69.7	11.2	0
Corn oil	12.7	24.7	57.8	0
Sunflower oil	11.9	20.2	63.0	0
Safflower oil	10.2	12.6	72.1	0
Canola oil	5.3	64.3	24.8	0

Source: Kays (1997).

oils. These essential fatty acids are members of the omega-6 and omega-3 fatty acid series.

Plant-derived foods do not contain significant amounts of cholesterol but do contain cholesterol-like steroids or phytosterols. These are present at highest concentrations in vegetable oils but may occur at appreciable levels in some horticultural crops. Fat-rich fruits and nuts, cauliflower, broccoli and carrots are good sources of phytosterols. They are absorbed only in trace amounts but inhibit the absorption of intestinal cholesterol (Jenkins et al., 2001). Clinical trials indicated that a daily intake of 0.8 g significantly reduced LDL and total cholesterol in the blood (Moruisi et al., 2006). Natural dietary intake varies from 167 to 437 mg per day (Ostlund, 2002). However, in vegetarian diets it may be as high as 1 g per day.

D Organic acids

Organic acids (OA), defined by the presence of carboxylic acid groups, are divided into aliphatic (straight chain) and aromatic acids. Citrate, malate and tartrate, the most abundant acids in fruits and vegetables, are aliphatic. Malate is the major acid in pome- and stone-fruit species, citrate is abundant in *Citrus*, berries and tomato, and tartrate is predominant in grapes. Aromatic organic acids occur in several fruits, but at relatively low concentrations. Benzoic acid is found in cranberries; quinic acid, in bananas and kiwifruit; and chlorogenic acid, in potatoes and eggplant. OAs may be further divided into mono-, di-, or tricarboxylic acids based on the number of carboxylic acid groups present. Citrate is a tricarboxylic acid, while malate and tartrate are both dicarboxylic. Lactic and acetic acids are monocarboxylic acids and are present in significant amounts in vegetables.

Fruits are normally more acidic than most vegetables. Except for lemons, acidity normally decreases with ripening. In clingstone peaches, citrate decreases faster than malate, while the opposite is true in apples and pears. Organic acid distribution within a fruit may not be uniform.

Organic acids (OAs) play an important role in fruit taste. The sugar to acid ratio is a widely used maturity index in citrus fruit. OAs can be incorporated into the tricarboxylic acid cycle (TCA), yielding ATP, but their energy contribution is minor. The main nutritional value of OAs is as a precursor for amino acid synthesis. Some nutritionally important compounds such as vitamin C are strictly organic acids. The major OAs present in fruit may help stabilize some vitamins and prevent the oxidation of phenolic compounds during processing.

E Digestible carbohydrates

After water, carbohydrates are the most abundant constituents in fruits and vegetables, accounting for 50–80% of dry weight. Carbohydrate functions include storage of energy reserves and they make up much of the structural framework of cells. Carbohydrates and proteins yield 4 kcal/g, while fats yield 9 kcal/g. Glucose and fructose are the most common simple sugars in fruits and the disaccharide sucrose, the primary transport form of carbohydrate in most plants, yields glucose and fructose upon hydrolysis. Glucose, fructose and sucrose are water-soluble and together are primarily responsible for the sweet taste of fruits and vegetables. In many fruits (apple, pear, strawberry, or grape), glucose and fructose are more abundant than sucrose, but in vegetables such as parsnip, beetroot, carrot, onion, sweet corn, pea and sweet potato and in some ripe fruits such as banana, pineapple, peach and melon, the sucrose concentration is higher. Other mono- and disaccharide sugars such as xylose, arabinose, mannose, galactose and maltose may also be present in small amounts (Salunkhe et al., 1991). Some fruits of the *Rosaceae* family have significant concentrations of the sugar alcohol sorbitol.

Total carbohydrate also includes starches, which are organized into small grains within chloroplasts or in specialized plastids, called amyloplasts. Some non-starchy root vegetables like parsnip, beetroot and carrot are rich in simple sugars: 8–18% of total carbohydrate.

F Dietary fiber

Definition and composition

Several definitions of fiber have been proposed, either physiological or based on the analytical method employed (Slavin, 2005). An expert panel defined the term "dietary fiber" as non-digestible carbohydrates and lignin in plants (Institute of Medicine, 2001). Dietary fiber includes very diverse macromolecules exhibiting a variety of physical-chemical properties. The main components of fiber are cellulose, cross-linking glycans (CGL), pectins, lignin, resistant starch and non-digestible oligosaccharides.

Cellulose

Cellulose is a main cell wall polymer consisting of β-1,4-linked glucose (Brett and Waldron, 1996). Individual glucan chains associate through hydrogen bonds to form highly stable microfibrils (Carpita and McCann, 2000). With the exception of avocado, in which the whole cell wall is degraded (O'Donoghue et al., 1994), little change in cellulose concentration is observed during ripening (Brummell, 2006).

Cross-linking glycans (CLG)

Several alkali-soluble cell wall polymers are classified as cross-linking glycans or hemicelluloses (Brummell and Harpster, 2001). Primary cell walls contain 25–35% CLG (Carpita and McCann, 2000). The most common CLG in dicot species is xyloglucan, characterized by a backbone of β-1,4-linked glucose with α-1,6 linked xylosyl lateral chains. The pentose residues can be further decorated with galactose, arabinose and/or fucose (Brummell, 2006). Xylans are abundant CLGs in monocot species, with a backbone of β-1,4-linked xylose decorated with side chains of arabinose and/or glucuronic acid. Other hemicellulosic compounds, usually less abundant, include gluco-mannans, galacto-mannans and galacto-gluco-mannans (Carpita and McCann, 2000).

Pectins

Pectins are also a diverse group, with a high proportion of galacturonic acid as a common feature (Ridley et al., 2001). Fruit tissues are particularly rich in pectins: they constitute up to 40% of the cell wall polysaccharides. The most abundant cell wall polyuronide is homogalacturonan, a homopolymer of α-1,4-linked galacturonic acid with variable degree of methyl esterification at C6 (Willats et al., 2001). The degree of polymerization and proportion of methyl esters affect pectin solubility. Pectins are deposited in the cell walls with a high degree of esterification that usually decreases during ripening. Another modification commonly observed in ripening fruits is reduced pectin polymer size (Brummell, 2006; Vicente et al., 2007b). The extent of pectin depolymerization is variable: avocado fruit undergo a dramatic decrease in polyuronide size (Huber and O'Donoghue, 1993), while negligible changes occur in peppers and some berries (Brummell, 2006; Vicente et al., 2007a). Rhamnogalacturonan I (RG I) and II (RG II) are also pectic polysaccharides present in plant cell walls. RGI has a backbone of alternating α-1,2-rhamnosyl and α-1,4-galacturonosyl residues (Willats et al., 2001) with side chains rich in arabinose and galactose (Carpita and McCann, 2000). Losses of side chain residues are common during fruit ripening and affect pectin solubility and hydration potential (Gross and Sams, 1984; Redgwell et al., 1997). RG II is the most complex cell wall polysaccharide and forms dimers via borate diester bonds (Kobayashi et al., 1996; O'Neill et al., 2004). Pectins extracted from citrus, apples and beets are used commercially to manufacture jams and jellies (Holzwarth et al., 2013).

Lignin

Lignin, along with cellulose and chitin, is one of the most abundant biopolymers in nature (Boerjan et al., 2003). It is an aromatic hetero-polymer formed by the association of three hydroxycinnamyl alcohol derivatives (*p*-coumaryl, coniferyl and sinapyl alcohols) (Srinivasa Reddy et al., 2005). It is a highly resistant polymer present in secondary cell walls and is associated with fibers, sclereids, xylem vessels, seed coats and pith of some fruits. Lignin is present in most fruits and vegetables at low levels, but in some commodities it can negatively impact quality. Toughening of asparagus spears during storage is related to increased lignin deposition (Saltveit, 1988; Huyskens-Keila and Herppichb, 2013; Janositz et al., 2011).

Resistant starch

Starches are polysaccharides: glucosyl residues linked by α-D-(1-4) and/or α-D-(1-6) linkages (Sajilata et al., 2006). Resistant starch and its degradation products are not digested in the small intestine (Asp, 1994). Such starches can be fermented by large intestine microflora, producing products that may provide physiological benefits (Mudgil and Barak, 2013; Laurentin and Edwards, 2013). Legumes are rich in resistant starch; up to 35% of this polysaccharide could escape digestion (Marlett and Longacre, 1996). Unripe bananas, green mango and potato are also relatively rich in resistant starch. Overall, little information is available about resistant starch concentrations in foods and the amount of resistant starch in a typical diet (Dodevska et al., 2013; Chung et al., 2011; Fuentes-Zaragoza et al., 2010).

Non-digestible oligosaccharides (NDOs)

Oligosaccharides are low-molecular-weight carbohydrates, intermediate between simple sugars and polysaccharides (Mussatto and Mancilha, 2007). While several oligosaccharides are hydrolyzed in the digestive tract, others resist digestion. Examples include raffinose (a trisaccharide of galactose, fructose and glucose), stachyose (two galactosyl units with one glucosyl and one fructosyl sequentially linked) and verbascose (three galactosyl, one glucosyl and one fructosyl unit sequentially linked). Among horticultural commodities, legumes are rich in NDOs (Mussatto and Mancilha, 2007).

Benefits of fiber intake

One of the best-known benefits of dietary fiber is its modulation of the intestinal function (Institute of Medicine, 2001). Fiber-rich meals promote satiety earlier, usually have fewer calories and can assist weight control (Marlett et al., 2002). Undigested dietary fiber is fermented in the colon to form acetic, propionic and butyric acids which participate in satiety signaling (Martin et al., 2013). High fiber intake is associated with disease prevention (Meyer et al., 2000; Institute of Medicine, 2001), reduced serum cholesterol and blood pressure and lower risk of coronary disease (Rimm et al., 1996; Wolk et al., 1999). Increasing viscous fruit and vegetable fiber and whole grains improves glycemic control and bodyweight management (Martin et al., 2011). Total fruit and vegetable consumption was inversely associated with colorectal cancer risk (Terry et al., 2001). Fiber may reduce the bioavailability of some phytochemicals or may be reduced by binding or entrapment (Palafox-Carlos et al., 2011). National dietary guidelines recommend increasing dietary fiber intake to 20−35 g per day; the average fiber intake of United States adults is less than half of this (Marlett and Slavin, 1997; Casiglia et al., 2013).

Sources of fiber

Whole grains, fruits and vegetables are good sources of fiber (Anderson et al., 2007). In 2004, fruits and vegetables contributed 37.1% of the fiber in the food supply, followed by grain products (36.0%) and legumes (13.3%) (Hiza and Bente, 2007). Fruits and vegetables average 1−3% fiber on a fresh weight basis (Table 5.2). Nuts, legumes and dried fruits are particularly rich in fiber. Fiber properties differ greatly depending on the food source. For instance, pectin is low in grains, but constitutes ∼20−35% of total fiber in fruits, vegetables, legumes and nuts. Cross-linking glycans account for about half of the total fiber in grains and ∼25−35% of total fiber in other foods. Cellulose is one-third; or less of total fiber in most foods (Marlett, 1992).

Relevant properties of dietary fiber include particle size and bulk volume, surface area characteristics, water absorbing capacity, viscosity and the ability to

Table 5.2 Fiber Content of Selected Fruits, Vegetables and Nuts

Product	Dietary fiber (%)
Almond	12.2
Apple	2.4
Asparagus	2.1
Avocado	6.8
Banana	2.6
Broccoli	2.6
Carrot	2.8
Kiwifruit	3.4
Lettuce	2.1
Onion	1.7
Orange	2.4
Pea	2.6
Peach	1.5
Peanut	8.5
Pear	3.1
Pepper	2.1
Pineapple	1.4
Plum	1.4
Potato	2.2
Prune	7.1
Raisin	3.7
Spinach	2.2
Strawberry	2.0
Tomato	1.2
Walnut	6.7

Source: U.S. Department of Agriculture (2008).

adsorb or entrap minerals and organic molecules (Guillon and Champ, 2000). The main modifications in fiber during storage are increased solubility and reduced molecular size by several cell wall-loosening enzymes (Brummell, 2006; Fisher and Bennett, 1991). In some commodities (e.g., celery), excessive fiber is potentially detrimental. Processing or home preparation of fruits and vegetables does not cause major losses of fiber (Zyren et al., 1983).

G Vitamins

Vitamins are required in trace amounts for normal development that cannot be synthesized in sufficient quantities by an organism, and must be obtained from the diet. The term "vitamin" derives from "vital amine" because the first vitamin discovered (thiamine) contained an amino group. The vitamins known today are vitamin A (retinol), the B complex [B1 (thiamine), B2 (riboflavin), B3 (niacin), B5 (pantothenic acid), B6 (pyridoxine), B9 (folate/folic acid), biotin, choline and B12 (cyanocobalamine)] and vitamins C, D, E and K. They do not have common functions or structure and are usually classified as fat-soluble (A, D, E and K) or water-soluble (B complex and C) (Salunkhe et al., 1991). Fruits and vegetables are a vital source of vitamins, but concentrations vary among species, cultivars, environmental conditions and cultural practices (Rodriguez-Amaya, 2001; Asensi-Fabado and Munné-Bosch, 2010; Moretti et al., 2010; Tiwari and Cummins, 2013).

Pro-vitamin A

Carotenoids are liposoluble pigments responsible for the yellow, orange and red colors of several fruits and vegetables. They are terpenoids formed by eight isoprene units (2-methyl-1,3-butadiene) derived from isopentenyl diphosphate. Those having an unsubstituted β-ring with an 11-carbon polyene chain have pro-vitamin A activity (Meléndez-Martínez et al., 2007), like α-carotene, β-carotene and cryptoxanthin (Kopsell and Kopsell, 2006). The structural requirement is satisfied by ~60 carotenoids (Rodriguez-Amaya, 2001). Vitamin A plays a crucial role in vision, cell division and differentiation, bone development and reproduction. Adult daily vitamin A requirement is estimated at 5000 international units (1 IU = 0.3 μg retinol or 0.6 μg β-carotene). Vitamin A deficiency is particularly frequent in populations where diets are based almost exclusively on a single, starch-based crop deficient in pro-vitamin A carotenoids (Mayer et al., 2008). Vitamin A deficiency is estimated to affect ~1/3 of children under the age of five worldwide, a significant number of whom suffer blindness or die (Cuttriss et al, 2011; Fernández-García et al., 2012).

Carotenoids are further subdivided into two classes: carotenes containing C and H (e.g., α-carotene, β-carotene, lycopene) and oxygenated derivatives known as xanthophylls (lutein, violaxanthin, zeaxanthin). In plants, carotenoids have functions related to light capture in the blue–green region of the spectrum and subsequent transfer to the photosynthetic centers (Kopsell and Kopsell, 2006). They also protect photosynthetic structures from photo-inhibition (Grusak and Della Penna, 1999). Carotenoids are usually present at low concentrations that are highly variable among species. Fruits and vegetables provide 30% of the vitamin A in the American diet (Hiza and Bente, 2007). Vegetables that supply useful amounts of carotene include carrots, pumpkins and squashes. Fruits are generally less good sources, with a few notable exceptions like apricot, mango, citrus, papaya and watermelon (Table 5.3). Tomato and pepper also contain high concentrations of carotenoids, especially in the peel (Rodriguez-Amaya, 2001). More than 600 different carotenoids have been identified, but a small group is usually prevalent. Beta-carotene, the most studied carotenoid, accumulates in carrots. Lycopene is abundant in tomato and watermelon. Other carotenoids found in fruits and vegetables include α-carotene, lutein, cryptoxanthin and zeaxanthin. In

Table 5.3 Carotene Concentration (Mean Values) of Selected Fruits

Product	Carotene (μg/100 g)
Mango	1800
Cantaloupe	1000
Pawpaw	810
Guava	435
Apricot	405
Plum	295
Watermelon	230

Source: Rodriguez-Amaya (2001).

tomato and peach, carotene biosynthesis continues after harvest. There is little difference in carotene between cooked and raw vegetables, but food preparation may affect carotene availability. Carrot puree allows better absorption than shredded or whole carrots. Absorption of carotene is more effective if the diet includes at least 15% fat.

Vitamin B complex

Thiamine pyrophosphate is a co-factor, present in all living systems, that catalyzes several biochemical reactions. It is particularly important in carbohydrate metabolism. A daily intake of 1–2 mg is recommended for adults. Legumes are especially rich in thiamine. Compared to other vitamins such as ascorbic acid, thiamine is relatively stable at cooking temperatures, especially in a slightly acidic solution. However, losses of 25–40% may occur.

Riboflavin is the central component of flavoproteins. The average human requires ~1–2 mg/day. Green vegetables such as bean, beet, pepper and spinach are particularly good while starchy vegetables and fruits are relatively poor sources of riboflavin. Niacin, or nicotinic acid, is a precursor of NADH, NAD, NADPH and NADP, which play essential roles in living organisms. A daily intake of 10–15 mg niacin is recommended. Niacin can be synthesized in the body from tryptophan. Almonds are a good source, but the best are cape gooseberries and avocadoes. The stability of niacin in food is better than vitamins C and A. Unlike vitamins A and D, niacin cannot be stored for long periods (10–14 days) in the body. Consequently, deficiency symptoms can develop rapidly with improper intake (Martin et al., 2011).

Vitamin B_6 (pyridoxal phosphate) is a co-factor in many transamination, decarboxylation and deamination reactions (e.g., formation of ACC by ACC synthase in plants requires pyridoxal phosphate as a co-factor) (Ramalingam et al., 1985). It is present in appreciable amounts in bean, cabbage, cauliflower, spinach, sweet potato, grape, avocado and banana and is fairly heat stable.

Pantothenic acid can be obtained from fresh, canned or frozen fruits and vegetables. It occurs widely in peas, beans, nuts, broccoli, mushrooms, potatoes and sweet potatoes. Pantothenic acid deficiency leads to fatigue, headaches, sleep disturbances, tingling of hands and impaired immune responses. Biotin is stable during cooking, processing and storage of fresh, canned and frozen fruits and vegetables. However, it is synthesized in the intestinal tract (Salunkhe et al., 1991). Folic acid is essential for reproduction and normal growth (Bar-Oz et al, 2008). It is present in fruits, spinach, cabbage and other green vegetables. Choline is heat stable and occurs in dried legumes and vegetables. Choline deficiency in humans has never been reported. Vitamin B_{12} does not occur in fruits and vegetables.

Vitamin C

Ascorbic acid (AsA) and its first oxidation product dehydroascorbic acid (which is reduced in the human body) are both considered to be vitamin C. AsA is a water soluble, carbohydrate-derived compound with antioxidant and acidic properties due to a 2,3-enediol moiety (Figure 5.1). Humans and a few other species cannot synthesize AsA (Chatterjee, 1973) because the gene coding for the last enzyme in the pathway (L-gulono-1,4-lactone oxidase) is not functional (Valpuesta and Botella, 2004). Plants synthesize AsA via a pathway that uses L-galactose as a precursor (Smirnoff and Wheeler, 2000; Smirnoff, 2000). Another pathway using galacturonic acid recycled from cell wall pectin degradation is present in plants (Agius et al., 2003). AsA is involved in collagen biosynthesis (Murad et al., 1981). Even though nutritional deficiencies are rare in modern western cultures, it is generally recognized that dietary AsA has important health benefits (Carr and Frei, 1999; Hancock and Viola, 2005). In meat-poor diets, dietary AsA can improve iron uptake (Frossard et al., 2000). The recommended dietary allowance of vitamin C is 75 and 90 mg per day for men and young women, respectively (Levine et al., 2001).

Fruits, vegetables and juices are the main dietary sources of vitamin C. Fruits and vegetables account for 90% of the vitamin C in the United States food supply (Hiza and Bente, 2007). Vitamin C concentration varies depending on the commodity (Noctor and Foyer, 1998), from 1 to 150 mg/100 g FW (Lee and Kader, 2000).

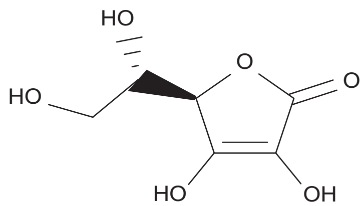

FIGURE 5.1

Structure of ascorbic acid, a main antioxidant present in fruits and vegetables.

Table 5.4 Vitamin C Concentration (Mean Values) of Selected Fruits

Product	Vitamin C (mg/100 g)
Guava, raw	184
Kiwi, raw	118
Litchi, raw	72
Pawpaw, raw	62
Strawberry, raw	57
Citrus fruits	31–53
Cantaloupe	42

Source: Salunkhe et al. (1991).

In berry fruits, AsA ranges from 14 to 103 mg/100 g FW (Pantelidis et al., 2007). Several tropical fruit species and leafy vegetables are rich in ascorbic acid, particularly rosehip, jujube and guava (see also Chapter 11). Other good sources include persimmon, strawberry, kiwifruit, peppers, citrus fruit, spinach, broccoli and cabbage (Table 5.4). Wide variations in vitamin C concentrations may exist among cultivars or species of the same genus: in one study, AsA in *Actinidia* species varied from 29 to 80 mg/100 g FW (Nishiyama et al., 2004). For any given product, AsA concentrations may vary due to genetic and environmental factors (reviewed in Lee and Kader, 2000) (see also Chapter 20). Sunlight exposure is a main factor that determines the AsA concentration. In general, more sunlight received during growth increases ascorbic acid. Retention of AsA is also affected by storage and processing conditions. Potatoes lose up to 80% of their original AsA over nine months' storage. AsA stability is reduced at high temperatures and bruising increases AsA degradation. Ascorbic acid is highly susceptible to oxidation, either directly or through the enzyme ascorbate oxidase (Sanmartin et al., 2007). The first oxidation product of AsA, dehydroascorbic acid, still has vitamin C activity, but this is lost on further oxidation (Salunkhe et al., 1991). When vegetables are cooked, high losses of vitamin C are expected. Starchy vegetables lose 40–80% of the vitamin C during cooking due to leaching and oxidation. Losses can be reduced by steam cooking. Freezing reduces vitamin C content slightly, but during long-term frozen storage (12 months), significant losses may occur (33–55%) (de Ancos et al., 2000).

Vitamin E

Vitamin E includes tocopherols and tocotrienols. These compounds exist in eight forms (four tocopherols and four tocotrienols). All isomers have aromatic rings with a hydroxyl group that donates hydrogen atoms to reduce reactive oxygen species (ROS). The terms α, β, γ and δ refer to the number and position of methyl groups on the chromanol ring. Each form has vitamin E activity, but α-tocopherol is the most active (Figure 5.2). Vitamin E deficiency stunts growth. Vitamin E is most abundant in oily seeds, olives, nuts, peanuts, avocados and almonds.

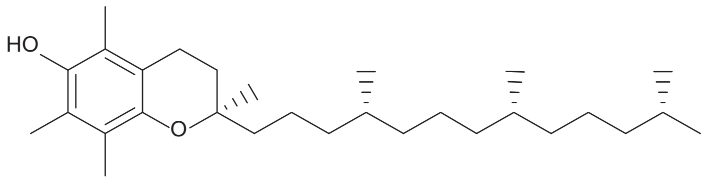

FIGURE 5.2

Structure of tocopherol.

Broccoli and leafy vegetables have less tocopherol than fats and oils, but are still better sources than other fruits and vegetables.

Vitamins D and K

Vitamin D promotes the absorption and use of calcium and phosphate. The main forms are ergocalciferol and cholecalciferol. They occur only in trace amounts in fruits and vegetables, but are found in fortified dairy products, eggs, liver and salmon (Hanson et al., 2013; Pludowski et al., 2013; Holick, 2013; Malone and Kessenich, 2008).

Vitamin K is essential for blood coagulation; the recommended daily intake is 120 μg. Dietary deficiency of vitamin K is uncommon. It is abundant in lettuce, spinach, cauliflower and cabbage, and it can also be produced by gut microflora (Presse et al., 2013).

H Minerals

Dietary minerals concern health specialists and consumers because of the number of processes they are involved in and continuous research highlighting the benefits of an adequate and balanced intake. Although there is no universally accepted definition or classification, the dietary focus on "minerals" derives from an interest in supporting the biosynthetic apparatus with required elemental components other than carbon, hydrogen and oxygen.

Minerals in food items are defined as the total ash content. The classification of many elements as essential minerals for human nutrition is not definitive, and there is still debate over the natural biological roles of vanadium, chromium, boron, aluminum and silicon in human health. Minerals are usually classified as macronutrients or micronutrients, based on the relative concentrations of each nutrient considered adequate for normal tissue function. Macronutrients include potassium (K), calcium (Ca), magnesium (Mg), nitrogen (N) and phosphorus (P), and their concentrations in plant tissues range from 1000 to 15,000 μg/g dry weight. Micronutrient concentrations are 100- to 10,000-fold less than those of macronutrients. Mineral micronutrients considered essential for human nutrition include manganese (Mn), copper (Cu), iron (Fe), zinc (Zn), cobalt (Co), sodium (Na), chlorine (Cl), iodine (I), fluorine (F), sulfur (S) and selenium (Se). Macronutrients

Table 5.5 Fruit and Vegetable Sources of Potassium, Ranked by Mg Potassium/ Standard Amount, also Showing Calories in the Standard Amount*

Fruits and Vegetables, Standard Amount	Potassium (mg)	Calories
Sweet potato, baked, 1 potato (146 g)	694	131
Tomato paste, 1/4; cup	664	54
Beet greens, cooked, 1/2; cup	655	19
Potato, baked, flesh, 1 potato (156 g)	610	145
White beans, canned, 1/2 cup	595	153
Tomato puree, 1/2 cup	549	48
Prune juice, 3/4 cup	530	136
Carrot juice, 3/4 cup	517	71
Lima beans, cooked, 1/2 cup	484	104
Winter squash, cooked, 1/2 cup	448	40
Banana, 1 medium	422	105
Spinach, cooked, 1/2 cup	419	21
Tomato juice, 3/4 cup	417	31
Tomato sauce, 1/2 cup	405	39
Peaches, dried, uncooked, 1/4; cup	398	96
Prunes, stewed, 1/2 cup	398	133
Apricots, dried, uncooked, 1/4; cup	378	78
Cantaloupe, 1/4; medium	368	47
Honeydew melon, 1/8; medium	365	58
Plantains, cooked, 1/2 cup slices	358	90
Kidney beans, cooked, 1/2 cup	358	112
Orange juice, 3/4 cup	355	85
Split peas, cooked, 1/2 cup	355	116

**U.S. Department of Health and Human Services and U.S. Department of Agriculture (2005).*
The dietary reference intake (DRI) for potassium for adults and adolescents is 4700 mg/day.

can also be classified into those that maintain their identity as ions within plant tissues (e.g., K^+, Ca^{2+} and Mg^{2+}) and those that are assimilated into organic compounds (e.g., N, P and S). In general, vegetables are a richer source of minerals than fruits (Table 5.5).

Minerals have both direct and indirect effects on human health. The direct effects of minerals are the consequences of their consumption by humans, while indirect effects are their impact on fruit and vegetable quality and subsequent consumer acceptance (see also Chapter 4). From a direct nutrition standpoint, potassium is the most abundant in both fruits and vegetables, but nitrogen and calcium have major impacts on food quality.

Until recently, nutrition research focused on single-mineral effects on human health, generally with incongruent results (Aaron and Sanders, 2013). The recognition that minerals are not consumed individually but as combined constituents of a varied diet has shifted efforts to unraveling the role of overall diet, or dietary patterns, in blood pressure, cardiovascular diseases, bone diseases and other chronic disorders. Epidemiological surveys suggest that total diet has more influence on health than specific components. It is increasingly clear that it is not only an excess or deficiency of a single mineral but also of multiple nutrients in combination that have dietary effects on health.

Fruits and vegetables are not recognized as primary sources of mineral nutrition (Fairweather-Tait and Hurrell, 1996). Nevertheless, the Dietary Approaches to Stop Hypertension (DASH) emphasize fruits, vegetables and low-fat dairy products as a source of minerals. In the DASH dietary pattern, vegetables contribute 14.3, 15.5, 16.2 and 10.4% of required calcium, magnesium, potassium and zinc, respectively (Lin et al., 2003). There has been a trend towards lower mineral contents in fruits and vegetables over the past decades (Mayer, 1997; Ekholm et al., 2007) which has not been fully offset by increased fruit and vegetable consumption. Vegetable contribution of potassium, phosphorus, magnesium, calcium, copper, iron and zinc to the United States food supply decreased significantly during the last century, while the fruit contribution of potassium, phosphorus, magnesium and copper increased (Table 5.6).

Strategies for improving our mineral intake from fruits and vegetables have been implemented. These comprise increasing the consumption of fruits and vegetables and increasing concentrations of essential nutrients through fortification. Alternative approaches include improving nutrient bioavailability and retention.

Table 5.6 Minerals (%) Contributed from Fruits and Vegetables to the U.S. Food Supply in Selected Years

	Fruit (Year/s)			Vegetables (Year/s)		
Mineral	**1909–1919**	**1960–1969**	**2004**	**1909–1919**	**1960–1969**	**2004**
Potassium	8.0	8.7	11.2	36.7	27.1	26.6
Calcium	2.6	2.2	2.6	8.7	6.0	7.0
Phosphorus	1.5	1.5	1.8	10.4	7.7	7.7
Magnesium	4.5	5.6	6.1	18.2	15.9	13.9
Copper	5.2	6.1	6.1	30.2	22.8	17.2
Iron	3.3	3.1	2.5	18.4	13.5	10.1
Zinc	1.2	1.3	1.2	9.1	7.4	6.4
Sodium	0.8	1.3	2.0	10.4	23.4	28.9
Selenium	0.5	0.6	0.4	1.2	2.4	2.3

Source: Hiza and Bente (2007).

Potassium (K)

A potassium-rich diet contributes to lower blood pressure, blunting the effects of NaCl (Salunkhe et al., 1991). Inadequate potassium intake has long been associated with higher blood pressure (McCarron and Reusser, 2001). Potassium also regulates heartbeat, assists in muscle contraction and is needed to send nerve impulses and to release energy from fat, carbohydrates and protein. Different nutrients and phytochemicals in fruits and vegetables, including potassium, may independently or jointly reduce cardiovascular disease risk (Ignarro et al., 2007). Potassium is a systemic electrolyte that co-regulates ATP with sodium. Potassium favorably affects acid–base metabolism, which may reduce the risk of developing kidney stones (Zerwekh et al., 2007), and possibly decreases bone loss with age. Although calcium intake is an important determinant of peak bone mass and in retarding bone loss in postmenopausal women, findings of higher bone mass and lower bone resorption in women with high intakes of potassium, magnesium, zinc and vitamin C emphasize the importance of considering the impact of other nutrients when focusing on a particular mineral (Cohen and Roe, 2000). Up to 11 different groups of compounds, vitamins, minerals, antioxidants among others, in fruits and vegetables could influence bone health (MacDonald, 2007).

Potassium is the most abundant individual mineral element in fruits and vegetables at between 60 and 600 mg/100 g FW. It is active in many cellular and whole plant functions: it serves as an osmoticum for cellular growth and stomatal function, balances the charges of anions, activates ~60 plant enzymes and participates in many metabolic processes, including protein synthesis, oxidative metabolism and photosynthesis. In fruits and vegetables, potassium occurs mainly in combination with organic acids. Examples of potassium-rich fruits and vegetables include bananas and plantains, leafy green vegetables, many dried fruits, oranges and orange juice, cantaloupes and honeydew melons, tomatoes and root vegetables (Table 5.7).

Calcium (Ca)

Calcium is essential for bone and tooth formation. Thus, calcium requirements are higher during adolescence. Calcium is also very important during later adulthood from a public health perspective, because inadequate calcium intake may increase the risk of osteoporosis, a condition in which decreased bone mass weakens bone (Nordin, 1997; Cohen and Roe, 2000). Nearly half of American women over 50 have low mineral bone density or osteoporosis and an estimated 1.3 million osteoporosis-related fractures occur each year at an estimated annual cost of a billion dollars (DeBar et al., 2004; Quesada-Gómez et al., 2013; Yesil et al., 2012; Emkey and Emkey, 2012) so osteoporosis prevention is a major public health target. Calcium fluxes are important mediators of hormonal effects on target organs through the phosphoinositol system and are closely linked with cyclic AMP systems. There is evidence linking hypertension to calcium deficiency (Appel et al., 1997; McCarron and Reusser, 2001).

Table 5.7 Mineral Composition of Some Fruits in mg/100 g FW

Fruit	Mineral									
	K	**Ca**	**Mg**	**P**	**Mn**	**Cu**	**Fe**	**Zn**	**Na**	**Se**
Apples, raw, with skin	107	6	5	11	0.035	0.027	0.12	0.04	1	0.0
Apricots, raw	259	13	10	23	0.077	0.078	0.39	0.2	1	0.1
Avocado, raw (California)	507	13	29	54	0.149	0.170	0.61	0.68	8	0.4
Avocado, raw (Florida)	351	10	24	40	0.095	0.311	0.17	0.4	2	–
Bananas, raw	358	5	27	22	0.270	0.078	0.26	0.15	1	1.0
Blackberries, raw	162	29	20	22	0.646	0.165	0.62	0.53	1	0.4
Blueberries, raw	77	6	6	12	0.336	0.057	0.28	0.16	1	0.1
Cherries, sweet, raw	222	13	11	21	0.070	0.060	0.36	0.07	0	0.0
Figs, raw	232	35	17	14	0.128	0.070	0.37	0.15	1	0.2
Grapefruit, raw, pink and red (California and Arizona)	147	11	9	12	0.020	0.032	0.08	0.07	1	–
Grapefruit, raw, pink and red (Florida)	127	15	8	9	0.010	0.044	0.12	0.07	0	1.4
Grapes, red or green (European type, e.g., “Thompson seedless”), raw	191	10	7	20	0.071	0.127	0.36	0.07	2	0.1
Kiwifruit, fresh, raw	312	34	17	34	0.098	0.130	0.31	0.14	3	0.2
Lemons, raw, without peel	138	26	8	16	0.030	0.037	0.60	0.06	2	0.4
Mangoes, raw	156	10	9	11	0.027	0.110	0.13	0.04	2	0.6
Melons, Cantaloupe, raw	267	9	12	15	0.041	0.041	0.21	0.18	16	0.4
Oranges, raw, California, “Valencia”	179	40	10	17	0.023	0.037	0.09	0.06	0	–
Papayas, raw	257	24	10	5	0.011	0.016	0.10	0.07	3	0.6
Peaches, raw	190	6	9	20	0.061	0.068	0.25	0.17	0	0.1
Pears, raw	119	9	7	11	0.049	0.082	0.17	0.10	1	0.1
Pineapples, raw, all varieties	109	13	12	8	0.927	0.110	0.29	0.12	1	0.1
Plums, raw	157	6	7	16	0.052	0.057	0.17	0.10	0	0.0
Pomegranates, raw	259	3	3	8	–	0.070	0.30	0.12	3	0.6
Raspberries, raw	151	25	22	29	0.670	0.090	0.69	0.42	1	0.2
Strawberries, raw	153	16	13	24	0.386	0.048	0.41	0.14	1	0.4
Watermelon, raw	112	7	10	11	0.038	0.042	0.24	0.10	1	0.4

U.S. Department of Agriculture (2008).

In plants, calcium is primarily associated with pectins. It has a major influence on the rheological properties of the cell wall and, consequently, on the texture and storage life of fruits and vegetables. Ca^{2+} can interact with anionic pectic polysaccharides, coordinating with the oxygen functions of two adjacent pectin chains to form the so-called "eggbox structure" and cross-linking the chains (Rose et al., 2003). Also, intracellular Ca^{2+} occupies a pivotal role in cell signal transduction (Sanders et al., 1999). Plant signals associated with Ca^{2+} signatures include wounding, temperature stress, fungal elicitors, oxidative stress, anaerobiosis, abscisic acid, osmotic stress, red or blue light and mineral nutrition. Transient increases in intracellular Ca^{2+} are often associated with initiation of responses. Thus, Ca^{2+} is a prominent second messenger and must be maintained in the cytoplasm at concentrations many orders of magnitude lower than in the cell wall.

Horticultural crops are a secondary source of calcium compared to dairy products, but fruits and vegetables account for almost 10% of the calcium in the United States food supply (Table 5.7; Cook and Friday, 2003). Dark green, leafy cabbage family vegetables and turnip greens are good calcium sources and most green leafy vegetables are potential sources of absorbable calcium (Jodral-Segado et al., 2003; Titchenal and Dobbs, 2007). Projects designed to test the efficacy of a health plan-based lifestyle intervention for increasing bone mineral density propose not only increased consumption of high-calcium foods, but also of fruits and vegetables (DeBar et al., 2004).

Magnesium (Mg)

Magnesium is important in protein synthesis, release of energy from muscle storage and body temperature regulation. It is critical for proper heart function and bone formation as previously described. Magnesium activates over 100 enzymes. In plants, the porphyrin-like ring structure of chlorophyll contains a central magnesium atom coordinated to the four pyrrole rings. Magnesium is also involved in energy metabolism as a constituent of the Mg-ATP or Mg-ADP complex. The Calvin cycle pathway that produces a three-carbon compound as the first stable product in the multistep conversion of CO_2 into carbohydrates is partially regulated via stromal Mg^{2+} concentration. This nutrient also serves important biochemical functions in protein synthesis (Mengel and Kirkby, 1982).

The vegetable contribution to total magnesium in the United States food supply was 14% (Table 5.6) (Allen, 2013; Zhang et al., 2012). Magnesium intake was less than adequate for both adults and children (Sigman-Grant et al., 2003). Mixed users, who are more likely to consume grains, fruit and dairy products, had higher magnesium densities than high-fat users, who consumed significantly more meat (Sigman-Grant et al., 2003). Generally, magnesium concentrations are significantly higher in vegetables than in fruits, while nuts are good sources of this nutrient. Overall, dry fruits and legumes are high in magnesium (Jodral-Segado et al., 2003).

Phosphorus (P)

Inorganic phosphate is essential for skeletal mineralization and for multiple cellular functions including glycolysis, gluconeogenesis, DNA synthesis, RNA synthesis, cellular protein phosphorylation, phospholipid synthesis and intracellular regulatory roles (DiMeglio et al., 2000). Phosphorus is a primary bone-forming mineral. Because most Westerners eat high-phosphate diets, isolated dietary phosphate deficiency is exceedingly rare except for occasional metabolic disorders such as hyperphosphatemia (DiMeglio et al., 2000).

Phosphorus exists in plants as both inorganic phosphate anions and organophosphate compounds (Raghothama, 1999). Unlike sulfate and nitrate, phosphate is not reduced during assimilation, but remains in its oxidized state, forming phosphate esters in a variety of organic compounds. Inorganic phosphorus is a main structural component of nucleic acids and phospholipids, plays a central role in energy conversion in the form of high-energy phosphoester and diphosphate bonds, is important as a substrate and a regulatory factor in oxidative metabolism and photosynthesis, participates in signal transduction and regulates the activities of an assortment of proteins through covalent phosphorylation/dephosphorylation reactions. Fruit and vegetable contribution to total phosphorus was 9.5% (Table 5.6). Among tree fruits, nuts are significant sources of phosphorus.

Nitrogen (N)

The largest requirement for nitrogen in eukaryotic organisms is for amino acid biosynthesis, building blocks of proteins and precursors of many other compounds. Proteins represent a large percentage of the human body and carry out many different cell functions. Therefore, protein synthesis is central to cell growth, differentiation and reproduction.

Nitrogen is also an essential component of nucleic acids, co-factors and other metabolites. Several plant hormones (indole-3-acetic acid, zeatine, spermidine) contain nitrogen or are derived from nitrogenous precursors. Alkaloids and other secondary compounds contain nitrogen and various phenolics derived from the amino acid phenylalanine. Nitrogen is also a major constituent of chlorophyll. The characteristic preharvest yellow color of nitrogen-starved vegetables – a physiological disorder called chlorosis – reflects their inability to synthesize adequate amounts of green chlorophyll under nitrogen-limiting conditions.

Sulfur (S)

Sulfur is an essential nutrient for growth, being primarily used to synthesize cysteine and methionine. These sulfur-containing amino acids are pivotal for structural and catalytic functions of proteins and are used to form numerous essential and secondary metabolites. Oxidized thiol groups of two cysteine residues form disulfide bonds; covalent linkages that establish tertiary and sometimes quaternary protein structures. The dithiol ↔ disulfide interchange can be a regulatory mechanism that mediates redox reactions.

Sulfur nutrition is important for species in the order Brassicales (e.g., white cabbage, broccoli, cauliflower, capers) to synthesize anticarcinogenic glucosinolate compounds (reviewed in Sozzi, 2001). In caper (*Capparis spinosa* L.), 160 flavor components were identified, including elemental sulfur (S_8) and >40 sulfur-containing compounds, among them thiocyanates and isothiocyanates. Although essential for human and plant life, sulfur is a relatively minor component compared to nitrogen. Generally, it is not a growth-limiting nutrient, since sulfate, the oxidized anion, is relatively abundant in the environment.

Manganese (Mn)

Manganese is a key component of some enzymes, including oxygen-handling enzymes. It supports brain function and reproduction and is required for blood sugar regulation. In addition, it is part of bone structure. Manganese is a co-factor for antioxidant enzymes like the mitochondrial superoxide dismutase.

In plants, manganese atoms undergo successive oxidations to yield a strongly oxidizing complex that can oxidize water during photosynthesis. Like magnesium, manganese is required in enzyme reactions involving carbon assimilation. Chloroplasts are most sensitive to manganese deficiency. Among horticultural crops, spinach is a good source of manganese (Pennington and Fisher, 2010).

Copper (Cu)

Copper, a redox-active metal, is critical for the oxidative defense system; oxidative stress is a characteristic of copper deficiency (Uriu-Adams and Keen, 2005). Copper is necessary to form hemoglobin and is a cofactor for over 30 proteins including superoxide dismutase, ceruloplasmin, lysyl oxidase, cytochrome c oxidase, tyrosinase and dopamine-β-hydroxylase (Arredondo and Núñez, 2005). During the past decade there has been increasing interest in the concept that marginal copper deficits (López de Romaña et al., 2011) can contribute to the development and progression of cardiovascular disease and diabetes. Deficits in this nutrient during pregnancy can cause gross structural malformations in the fetus and persistent neurological and immunological abnormalities in the offspring (Uriu-Adams and Keen, 2005).

In plants, copper is required for chlorophyll synthesis and several copper-containing enzymes that reduce molecular oxygen. As with other trace minerals, the availability of copper to plants decreases as the pH rises above seven. At high pH, copper is strongly adsorbed to clays, iron and aluminum oxides and organic matter. Of the micronutrients required by plants, copper often has the lowest total concentration in soil.

Between 1909 and 1919 in the United States, vegetables were the leading source of copper (30%). In 2004, grains (21%) and legumes, nuts and soy (20%) replaced vegetables (17%) as the leading sources of copper (Table 5.7; Hiza and Bente, 2007).

Iron (Fe)

The metabolic fates of copper and iron are intimately related. Their essential role resides in their capacity to participate in one-electron exchange reactions. Systemic copper deficiency generates cellular iron deficiency, which in humans results in diminished work capacity, reduced intellectual capacity, stunted growth, altered bone mineralization and compromised immune response. Iron is required in numerous essential proteins including heme-containing proteins, electron transport chain and microsomal electron transport proteins and iron–sulfur proteins, and in enzymes such as ribonucleotide reductase, prolyl hydroxylase phenylalanine hydroxylase, tyrosine hydroxylase and aconitase (Arredondo and Núñez, 2005; Guss et al., 2011; Pettit et al., 2011; Horowitz et al., 2013).

Iron is a constituent of the hem complex, a naturally occurring plant chelate involved in electron transfer in several important plant enzymes (Mengel and Kirkby, 1982). The plant plastid stroma may contain deposits of phytoferritin, an iron storage form similar to the ferritin of animal cells. Phytoferritin occurs almost exclusively in plastids, especially those of storage organs (Briat and Lobreaux, 1997). In vegetable green leaves, there is a good correlation between iron and chlorophyll concentrations. Inadequate iron nutrition results in abnormal chlorophyll development: deficiency begins as interveinal chlorosis on younger leaves, resulting in prominently green veins. The resultant reduced photosynthetic capability also reduces the weight and area of affected leaves. Description and causes of iron deficiency have been extensively reviewed for horticultural crops (Korcak, 1987).

Adult users of lower-fat foods consume more nutrient-dense diets and more iron (Kennedy et al., 2001; Sigman-Grant et al., 2003). The predominant source of iron in the American food supply is grain products, followed by meat, poultry and fish. Between 1909 and 1919, vegetables furnished 18% of the iron in the food supply, but in 2004 that share dropped to 10% (Table 5.6), partially due to less use of white potatoes after 1920. Although potatoes are not a good source of iron, their contribution increases when eaten in large quantities (Hiza and Bente, 2007), particularly if the skin is consumed: baked potato skin has 20-fold more iron than the flesh. Almonds, pistachio nuts, walnuts and pecans are good sources of iron. Green vegetables (parsley, broccoli, kale, turnip greens and collards) and legumes (green peas and beans) are also good sources of iron.

Zinc (Zn)

Zinc is a pervasive microelement that plays a catalytic or a structural role in >200 enzymes involved in digestion (carboxypeptidase, liver alcohol dehydrogenase, carbonic anhydrase), metabolism, reproduction and wound healing. Zn^{2+} is a cation with various coordination possibilities and several potential geometries. Thus, it easily adapts to different ligands. The main role of structural Zn^{2+} in proteins is to stabilize tertiary structures. In addition, zinc has a critical role in the immune response and is an important antioxidant.

Zinc activates many plant cell enzymes (Romheld and Marschner, 1991) but only a few (alcohol dehydrogenase, superoxide dismutase, carbonic anhydrase and RNA polymerase) contain the micronutrient. Zinc affects carbohydrate metabolism because Zn-dependent enzymes participate in biochemical reactions of sugars. Zinc also plays a role in maintaining cell membrane integrity, protecting from $O_2^{-\bullet}$ damage and synthesizing RNA and tryptophan, a precursor of indole-3-acetic acid. A comprehensive review of soil, plant and management factors associated with zinc nutrition of crops is available (Swietlik, 1999).

Fruits and vegetables account for only 1.2% and 6.4%, respectively, of the zinc in the American food supply (Hiza and Bente, 2007). As with magnesium, zinc intakes may be insufficient in both adults and children (Sigman-Grant et al., 2003). Fruits are poor in zinc, but pecans and walnuts are good sources.

Sodium (Na)

Sodium is important for electrolyte balance and blood pressure. Along with potassium, it co-regulates ATP. Sodium intake from vegetables increased during the last decades (Table 5.6), due to increased consumption of processed vegetables, largely tomatoes and white potatoes. Except for canned vegetables, food supply sodium estimates do not include sodium added in processing. Thus, the relative contribution of vegetables to sodium in the food supply is likely overstated (Hiza and Bente, 2007). Table salt (NaCl) is by far the main dietary source of sodium. Olives and spinach are horticultural sources of sodium. In general, fruits are poor in sodium and are recommended for low-sodium diets.

Factors influencing mineral content of fruits and vegetables

Species and cultivar

Mineral composition varies widely in raw fruits (Table 5.7) and vegetables. Leafy vegetables have higher concentrations of nutrients that are less mobile in the plant (e.g., calcium) and depend on direct water flow rather than recycling from older leaves. Tissues with higher transpiration rates generally have higher tissue calcium concentrations (Witney et al., 1990a). Mineral concentrations may vary widely among cultivars. For example, both “Dwarf Brazilian” bananas (Santa Catarina Prata, *Musa* sp. AAB) and “Williams” (Cavendish subgroup, *Musa* sp. AAA) are considered good sources of potassium. Nevertheless, “Dwarf Brazilian” bananas have more P, Ca, Mg, Mn and Zn than “Williams” bananas (Wall, 2006). In contrast, no strawberry variety was a superior source of minerals (Hakala et al., 2003).

As a result of the distribution of vascular tissue, sink characteristics and metabolic rates, higher mineral concentrations are usually found in the skin and seeds than in the flesh of fruits. Tissues with higher metabolic rates (epicarp, core) may accumulate more nitrogen and phosphorus. Rapidly expanding or large-celled tissues are unlikely to have high calcium concentrations. In mature fruit, the calcium concentration is highest in the peel (Saure, 2005).

Preharvest factors

Orchard location has important effects on fruit and vegetable mineral concentrations (Table 5.7). For example, potassium in bananas differs among locations/microclimates in Hawaii (Wall, 2006). Similar fluctuations in potassium among growing areas is seen in "Rainbow" papaya fruits (Wall, 2006).

Mineral composition fluctuates widely in raw fruits and vegetables due to preharvest factors (soil fertility, including both pH and concentrations of nutrients, soil moisture, growth temperature) and cultural practices (amount and timing of fertilization and irrigation, application of plant growth regulators, pruning and thinning of tree fruit species). Most agricultural practices are established primarily to increase productivity, not to improve human health, horticultural crop postharvest life or flavor (Crisosto and Mitchell, 2002). Usually, fertilizers are applied directly to the soil to raise nutrient concentrations that are inadequate for successful crop growth, and to maintain soil fertility, which will decline if nutrient removal from the soil via crop uptake, leaching, volatilization, or denitrification exceeds nutrients added via weathering of minerals and mineralization of organic matter. Nitrogen is the most frequently deficient element and most commonly applied fertilizer in orchards, while phosphorus and potassium are added when soil test results, plant response or tissue analysis indicate a need. N-P-K addition with irrigation water has several advantages, including the ability to transport soluble nutrients directly to the root zone whenever water is applied to the plant. Thus, fertilizer amounts and timing can be precise and adjusted to coincide more closely with actual plant demand. Calcium additions can be large when lime is applied to increase soil pH. Most micronutrients are rarely applied to soil but are sprayed directly on the canopy in dilute concentrations. In fruits, the quantity of nutrients absorbed through the waxy cuticle is often small relative to nutrient demand, but can ameliorate deficiency symptoms and improve fruit quality (Lysiak et al., 2008).

An excessive supply of nutrients relative to photosynthesis develops when the rate of nutrient assimilation is high relative to net photosynthesis. When this happens, nutrients can accumulate in fruits and vegetables to levels toxic for the plant or consumers. Excessive nitrogen leads to potentially harmful accumulations of nitrate in leafy greens and potatoes (Pavlou et al., 2007; Zhao et al., 2011). Such nutrient imbalances also affect crop quality.

Nutrient transport and source−sink relations also affect nutrient accumulation. For example, altered water economy affects calcium uptake, since calcium is transported mainly in the transpiration stream (Grange and Hand, 1987). Bagging fruit may decrease calcium concentrations and increase calcium-related disorders due to increased relative humidity (Witney et al., 1991; Hofman et al., 1997), although the evidence is inconclusive (Saure, 2005). Canopy position and crop load also influence calcium uptake. Tree vigor is usually associated with less calcium and magnesium in fruits (Witney et al., 1990a, b). Fruit from upper parts of the canopy tend to have less calcium (Ferguson and Triggs, 1990), and heavily cropped trees have fruit with more calcium and less potassium (Ferguson and

Watkins, 1992). Calcium transport to fruit is under hormonal control: gibberellins inhibit calcium translocation (Saure, 2005).

Tree size, spacing, row orientation, canopy shape and training system influence light distribution within fruit trees, which affects fruit mineral composition. In grapes, improving light penetration into the canopy increased anthocyanins and soluble phenols, but reduced potassium (Prange and DeEll, 1997). In kiwifruit, light promoted calcium accumulation (Montanaro et al., 2006). This finding was not fully explained by fruit transpiration: regulation by phytohormones could help determine calcium concentrations. The effect of sunlight is not universal: avocado fruit from the sunny side of trees had the same calcium levels as fruit from the shaded side (Witney et al., 1990b).

The mineral concentrations in some horticultural species are affected by intensive culture systems (glasshouse) or organic conditions. Tomato fruit contained more calcium and less potassium, magnesium and sodium when grown in an organic compost/soil mix than in hydroponic substrates (Premuzic et al., 1998). Organically cultivated apples, pears, potatoes and corn had higher mineral concentrations than conventionally cultivated ones (Smith, 1993). In contrast, Petersen and Pedersen (1991) found no differences in mineral concentrations between organically and conventionally cultivated vegetables. Organic cultivation did not affect strawberry mineral concentrations consistently (Hakala et al., 2003; Bedbabis et al., 2010).

Postharvest practices

Postharvest treatments with minerals, primarily calcium, can increase the storage life and quality of some fruits and vegetables. In the last decade, the industry has been encouraged to fortify food and beverages with calcium. Increasing the calcium concentration of horticultural crops gives consumers new ways to enhance calcium intake without supplements. In addition, phosphorous-free sources of calcium can help provide a good balance of dietary calcium and phosphorus (Martín-Diana et al., 2007).

There are two primary ways to apply postharvest calcium to horticultural crops: (1) dipping-washing, and (2) impregnation (Martín-Diana et al., 2007). Immersion treatments are used for fresh, sensitive products like leafy vegetables. The delicate texture of berries does not withstand vacuum infiltration, so dips in $CaCl_2$ solution are performed (García et al., 1996), followed by the removal of excess solution. Impregnation modifies the composition of food through partial water removal and replacement with solutes, without damaging integrity. The driving forces can be an osmotic gradient between sample and solution, application of vacuum followed by normal atmospheric pressure, or both. $CaCl_2$ is widely used as a firming agent and preservative for whole and fresh-cut fruits and vegetables (see also Chapter 10). Mineral concentrations were similar in fresh, canned and frozen fruit and vegetable products; this is expected, since these nutrients are inert and thus not sensitive to degradation by the thermal processes used in food preservation.

Incidence of minerals on fruit and vegetable quality and consumer acceptance

Consumers buy certain products as good sources of specific minerals: potato and sweet potato for potassium, banana for magnesium and potassium, spinach for iron, potassium, magnesium and as a non-dairy source of calcium. Mineral analysis is performed by ashing and atomic absorption (Pomeranz and Meloan, 1987). Without such advanced analytical equipment, the consumers cannot detect differences in individual products at the point of purchase (Institute of Food Technologists, 1990) (see also Chapter 14). Minerals are thus credence attributes because they cannot be detected by visual inspection or consumption. Thus, there is no incentive to measure minerals in a quality control program unless specific nutritional claims can be made.

To judge quality, consumers use purchase attributes (size, color, firmness, aroma and absence of defects) and consumption attributes (flavor and mouth feel) (see also Chapter 3). Many of these qualities are affected by mineral concentrations and are part of many factors leading to fruit and vegetable acceptability. Acceptability, defined as "the level of continued purchase or consumption by a specific population" (Land, 1988), determines the consumption of many essential nutrients: vitamins, antioxidants and fiber. Thus, the effect of minerals on crop quality and consumer acceptance should be considered. The effect of minerals on color, flavor, firmness and other attributes of specific horticultural commodities is described below.

Effect of minerals on color

In apples and pears, both leaf and fruit nitrogen positively correlate with fruit green background color (Raese, 1977; Marsh et al., 1996), regardless of the rootstock (Fallahi et al., 1985). Manganese is also associated with green ground color in apples (Deckers et al., 1997). Excessive nitrogen inhibits background color change from green to yellow, inhibits reddish blush development and decreases edibility in peaches (Sistrunk, 1985; Crisosto et al., 1995, 1997). High nitrogen also decreases fruit color in grapes (Kliewer, 1977). In *Citrus*, nitrogen retards endogenous chlorophyll catabolism (Koo et al., 1974) and postharvest ethylene may be required to accelerate de-greening. In apples, correcting potassium deficiency can increase fruit red color, but applications in excess of need have no effect (Neilsen and Neilsen, 2003). In tomato, potassium deficiency is associated with less lycopene and increased β-carotene (Trudel and Ozbun, 1971).

Effect of minerals on flavor

Nitrogen status correlates negatively with soluble solids in apples (Fallahi et al., 1985; Dris et al., 1999) and in pears (Raese, 1977). In contrast, soluble solids increase with increased nitrogen in tomatoes (Barringer et al., 1999). Apple calcium and phosphorus both correlated negatively with fruit soluble solids at harvest and after six months of 0°C storage, while fruit K/Ca ratio correlated positively with titratable acidity (Fallahi et al., 1985). In mango, total soluble solids increased when zinc sulphate fertilizer was applied to the soil (Bahadur et al., 1998). In "Fino 49" lemon, salinity reduced juice percentage and impaired juice quality by decreasing soluble solid sugars and titratable acidity (García-Sánchez et al., 2003). Reduced titratable acidity could be due to the accumulation of Cl^{-} instead of Na^{+}, a charge imbalance compensated by degradation of organic acids.

Minerals also affect the production of several classes of volatile compounds in pome fruit (reviewed in Mattheis and Fellman, 1999). In fresh onions, increased sulfur availability enhances pungency and total sulfur flavor but decreases the concentrations of precursors for synthesis of volatiles, imparting "green" and "cabbage" notes (Randle, 1997).

Effect of minerals on firmness

Excess nitrogen can decrease tissue firmness (Reeve, 1970; Prange and DeEll, 1997). Also, low phosphorus decreases firmness in low-calcium fruits (Sharples, 1980). The relationship between calcium and fruit firmness has been extensively studied and reviewed (Ferguson, 1984; Poovaiah et al., 1988; Harker et al., 1997; Sams, 1999). Higher firmness and/or slower softening after harvest/storage are associated with higher calcium concentrations or calcium applications in apples and pears (Fallahi et al., 1985; Raese and Drake, 1993, 2000a, b, 2002; Gerasopoulos and Richardson, 1999; Benavides et al., 2001), kiwifruit (Hopkirk et al., 1990; Gerasopoulos and Drogoudi, 2005) and strawberries (Chéour et al., 1990). Calcium foliar sprays on peaches and nectarines increased calcium slightly (Manganaris et al., 2005a, 2006). In California, no consistent effect on the quality of mid- or late-season peaches and nectarines was found (reviewed in Crisosto et al., 1997).

Postharvest calcium treatments can retain fruit firmness in apples (Wang, et al., 1993; Conway et al., 1994), peaches (Manganaris et al., 2005b, 2007; Lysiak et al., 2009), strawberries (Morris et al., 1985; García, et al., 1996), lemons (Valero et al., 1998; Martínez-Romero et al., 1999) and sliced pears and strawberries (Rosen and Kader, 1989). Calcium effects on fruit firmness are attributable to calcium's ability to cross-link with pectic polysaccharides by ionic association. Calcium binding may reduce the accessibility of cell wall degrading enzymes to their substrates.

Effect of minerals on rots, physiological disorders and nutritional value

Calcium-treated fruit has increased firmness and reduced rot incidence. Calcium may affect both processes through its role in strengthening plant cell walls (García et al., 1996; Fallahi et al., 1997; Conway et al., 1999). High nitrogen increases susceptibility to decay caused by *Monilinia fructicola* (brown rot) in nectarines (Daane et al., 1995). Wounded and inoculated "Fantasia" and "Flavortop" nectarines from trees with more than 2.6% leaf nitrogen were more susceptible to *M. fructicola* than fruit from trees with less leaf nitrogen (Michailides et al., 1993).

Consumers consider that fruits have less predictable quality than manufactured snacks. The effect of nutrients on the final quality of horticultural products may not become evident until harvest, distribution or consumption. The expression "latent damage" was coined by Peleg (1985) and later defined by Shewfelt (1986) as "damage incurred at one step but not apparent until a later step" to describe this quality loss. Physiological disorders are a type of latent damage. Some physiological disorders are related to nutrient imbalance. Calcium is the nutrient most commonly associated with postharvest disorders. Calcium deficiency is an important preharvest factor for fruit and vegetable physiological disorders such as bitter pit in pome fruit, blossom-end rot in tomato, blackheart in celery, cracking and cavity spot in carrot and tipburn in lettuce and cabbage (reviewed in Ferguson et al., 1999), although some authors question the role of calcium in these disorders (Saure, 1998, 2001). Other calcium-related disorders are associated with long-term cold storage, such as chilling injury (CI) in muskmelon (Combrink et al., 1995) and avocado (Chaplin and Scott, 1980). Postharvest calcium applications limited the incidence of chilling injury (CI) in peach fruit, expressed as flesh browning, after four weeks cold storage at 5°C and additional ripening at room temperature for five days (Manganaris et al., 2007). Nevertheless, preharvest calcium applications did not affect the onset of CI in peaches and nectarines (reviewed in Lurie and Crisosto, 2005).

Magnesium and potassium are part of an index to predict bitter pit (Bramlage et al., 1985; Autio et al., 1986). Fallahi and Righetti (1984) considered the ratio of nitrogen and calcium as an important component of a diagnosis and recommendation system (DRIS) for apple. High rates of nitrogen application exacerbated the incidence of physiological disorders, such as apricot pit burn (Bussi and Amiot, 1998, 2003).

Minerals can influence the concentrations of other nutrients in horticultural crops. Nitrogen fertilizers applied at high rates decrease the concentration of vitamin C in fruits (citrus juices) and vegetables (potatoes, cauliflower, white cabbage and crisphead lettuce), while increased potassium fertilization increases ascorbic acid (reviewed in Lee and Kader, 2000).

III Antioxidants

A Oxidative damage and antioxidants

Reactive oxygen species (ROS) are partially reduced forms of oxygen such as singlet oxygen, hydrogen peroxide (H_2O_2), superoxide ($O_2^{-\bullet}$) or hydroxyl radical ($OH^{-\bullet}$) (Asada, 1999; Mittler, 2002). ROS cause deleterious modifications in proteins, lipids and nucleic acids by altering normal metabolism in living organisms (Waris and Ahsan, 2006; Jeremy et al., 2004). The protective effects of fruit and vegetables are attributed in part to the presence of antioxidants (Cao et al., 1996; Wang et al., 1996). Antioxidants are compounds that prevent uncontrolled cellular

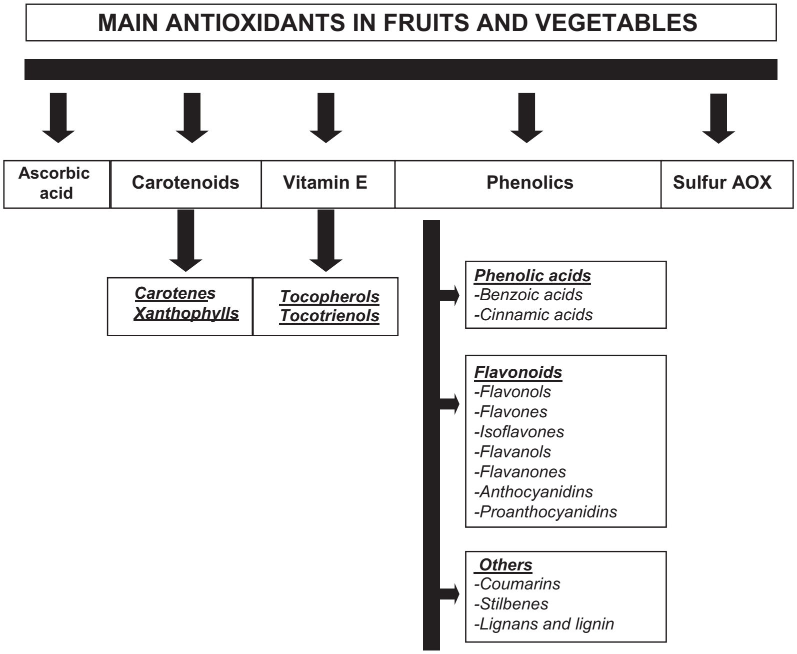

FIGURE 5.3

Main dietary antioxidants present in fruits and vegetables.

oxidation (Ames et al., 1993; Dragsted, 2003). They are present in all plant organs and include metabolites such as ascorbic acid, carotenoids, vitamin E, phenolics, glucosinolates and thiosulfinates (Figure 5.3).

B Ascorbic acid

Ascorbic acid is one of the most important compounds for human nutrition present in fruits and vegetables (Larson, 1988). Besides its vitamin functions, the role of AsA in disease prevention is associated with its capacity to neutralize ROS.

C Carotenoids

Fruits and vegetables are the main sources of carotenoids (Rao and Rao, 2007). The presence of conjugated double bonds in carotenoids is central to their antioxidant properties (Sandmann, 2001) and potential for preventing some diseases. They reduce LDL cholesterol oxidation, protecting against cerebral infarction, acute coronary events and stroke (Rinassen et al., 2001). Lycopene and β-carotene are the most studied carotenoids and protect against some digestive disorders (Kris-Etherton et al., 2002; Tan et al., 2010). The general properties of carotenoids were described above.

D Tocopherols and tocotrienols

Tocopherols and tocotrienols are fat-soluble compounds with vitamin E activity. Their distribution in fruits and vegetables was described above.

E Phenolic compounds

Phenolics are diverse compounds derived from aromatic amino acids. Their distinctive feature is the presence of aromatic rings with variable degrees of hydroxylation (Mattila et al., 2006). They contribute to fruit pigmentation and act as predator deterrents and antimicrobials. Phenolic compounds contribute to astringency and impart bitter taste in some products. They may also protect plant tissues against excessive UV radiation. They can be oxidized by plant peroxidases (PODs) and polyphenol oxidases (PPOs), leading to undesirable tissue browning. They are generally present at low concentrations, but in blueberries, levels can be over 0.1%. Phenolics accumulate preferentially in the peel, but this varies depending on species and chemical group. Eggplant anthocyanins are concentrated in the peel, while chlorogenic acid, the main antioxidant, predominates in the pulp, surrounding the seeds. As with other compounds, the health-promoting effects of phenolics depend on their bioavailability (Duthie et al., 2003; Seeram et al., 2006; Konic Ristic et al., 2011), but paradoxically their concentration in plasma is usually very low (Manach et al., 2005). Many phenolic compounds have been identified in plants (Tsao and Deng, 2004). They are grouped into sub-classes such as phenolic acids, flavonoids, lignans, stilbenes, tannins, coumarins and lignin.

Phenolic acids

Phenolic acids are derivatives of benzoic and cinnamic acids (Benbrook, 2005) (Figure 5.4). The most abundant benzoic acid derivatives are *p*-hydroxybenzoic, vanillic, syringic and gallic acids, while common cinnamic acid derivatives include *p*-coumaric, caffeic, ferulic and sinapic acids. The derivatives differ in the degree of hydroxylation and methoxylation of the aromatic ring. Caffeic acid is the most abundant phenolic acid in berry fruits (Mattila et al., 2006), while coumaric acid is usually present at lower concentrations (Rice-Evans et al., 1997). Ferulic acid comprises 90% of total phenolic acids in cereals (Manach et al., 2004; Scalbert and Williamson, 2000).

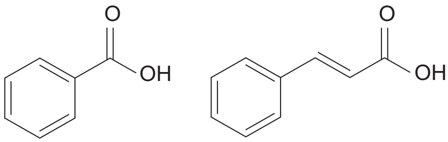

FIGURE 5.4

Structure of benzoic acid (left) and cinnamic acid (right), precursors of the two main classes of phenolic acids present in fruits and vegetables.

Flavonoids

Flavonoids are a large group of phenolic compounds with two aromatic rings associated by a 3 C oxygenated heterocycle. They are usually present as glycosides, which are more soluble than the corresponding aglycons, and are compartmentalized into the vacuoles (Rice-Evans et al., 1997). There are different flavonoid sub-classes: flavones and flavonols, flavanones and flavanols, isoflavones, proanthocyanidins and anthocyanidins (Le Marchand, 2002).

Flavones and flavonols

Flavonols have a central 3-hydroxypyran-4-one ring (Rice-Evans et al., 1997). Flavones lack the OH in position 3 (Figure 5.5). Rutin, luteolin and apigenin are common flavones, while the most abundant flavonols are quercetin and kampferol (Manach et al., 2004). Onions are rich in quercetin. Blueberries also have high concentrations, especially in peel, because their biosynthesis is stimulated by light exposure. Celery is a good source of flavones. In citrus, they are also abundant, but mainly in the peel.

Flavanones and flavanols

Flavanones have no double bond in position 2,3 of the central ring, while flavanols lack a carbonyl group at position 4 (Figure 5.6). The genus *Citrus* accumulates flavanone glycosides. Orange juice contains the flavanone glycoside

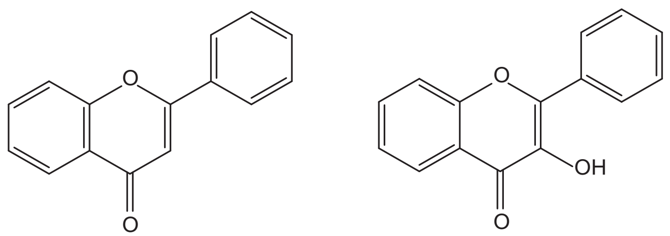

FIGURE 5.5

General structure of flavones (left) and flavonols (right).

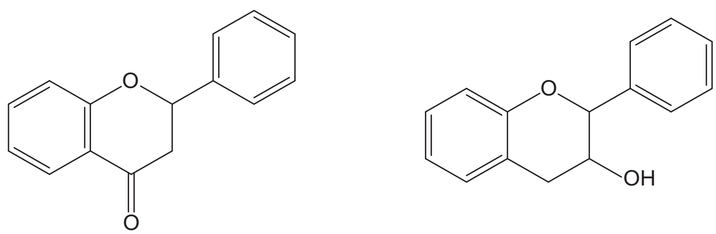

FIGURE 5.6

General structure of flavanones (left) and flavanols (right).

hesperidin (Tripoli et al., 2007). The flavanols catechin and epicatechin are common in grape (Rice-Evans et al., 1997).

Isoflavones

Isoflavones are phytoestrogens present in legumes. Soybean products are a good source of these compounds (Manach et al., 2004). The three most common isoflavones are genistein, glycitein and daidzein.

Proanthocyanidins

Proanthocyanidins are oligomeric flavonoids (usually dimers or oligomers of catechin and epicatechin). They are common in the peel and seeds of grape (Gu et al., 2004). Other sources include apple, almond and blueberry.

Anthocyanidins

The term anthocyanin is derived from the Greek words *anthos* and *cyan*, meaning flower and blue, respectively. They are pigments that provide the characteristic red or purple colors to some fruits. However, some forms are uncolored. Anthocyanidins contribute significantly to the antioxidant capacity of fruits and vegetables (Table 5.8). Because of their widespread distribution, anthocyanins are common antioxidants in the human diet. The *in vitro* antioxidant capacity of anthocyanins is associated with their ability to donate an H atom from an aromatic hydroxyl group to the free radicals and to delocalize an unpaired electron. The basic structure of anthocyanidins is derived from the flavilium cation (2-phenyl-benzopyril). Owing to their polarity, anthocyanins are readily soluble in water.

Six anthocyanidins are commonly found in fruits and vegetables: pelargonidin, cyanidin, delphinidin, peonidin, petunidin and malvidin. They differ in the substituents (OH, H or OCH_3) associated with the phenolic rings. Their distribution in fruits is: cyanidin 30%, delphinidin 22%, pelargonidin 18%, peonidin 7.5%, malvidin 7.5% and petunidin 5% (Andersen and Jordheim, 2006). Hydroxyl

Table 5.8 Fruits and Vegetables Particularly Rich in Specific Antioxidant Groups

Ascorbic acid	Vitamin E	Carotenoids	Phenolics
Strawberry	Almond	Pineapple	Blueberry
Pepper	Corn	Plum	Plum
Kiwifruit	Broccoli	Peach	Raspberry
Orange	Spinach	Pepper	Strawberry
Pepper	Peanut	Mango	Apple
Broccoli	Avocado	Melon	Blackberry
Guava		Tomato	
Rosehip		Carrot	
Persimmon			

distribution influences both the hue and antioxidant capacity of anthocyanidins. As a general rule, hydroxylation induces a shift of the visible max toward longer wavelengths (bathochromic effect, also known as blueing effect) (Gómez-Míguez et al., 2006). Methylation of hydroxyl groups causes the reverse trend. Consequently, the anthocyanidins with more hydroxyls are bluish, while those with methoxyl groups are red (Delgado-Vargas and Paredes-López, 2003). They are usually glycosylated or acylated, which increases or reduces their solubility, respectively. Sugars may be present as mono-, di- or trisaccharides. The major form of anthocyanins in most fruits is the monoglycoside, usually 70–100% of the total. Glucose, galactose, rhamnose and arabinose are the most common sugars in anthocyanins. Acylating agents include caffeic, *p*-coumaric, ferulic and sinapic acids (Castañeda-Ovando et al., 2009). These forms make up 0–6% of the total, except for blackberries and blueberries, in which they can be 15% (Wu et al., 2006). Anthocyanins form co-pigments with some metallic ions or colorless organic compounds in complex associations. Such interactions may change pigment hues and increase intensity (Boulton, 2001). Anthocyanin color is affected by pH. At low pH, the flavylium cation contributes purple and red colors. At higher pH (2–4), the quinoidal blue species predominate. Anthocyanin concentrations range from undetectable levels up to 611 mg/100 g FW in bilberries (Table 5.9). The structural diversity of anthocyanins in fruits has been analytically described in a recent review (Goulas et al., 2012).

Others

Lignans are diphenolic structures formed by the association of two cinnamic acid derivatives (Liu, 2007). They are present in linseed, cereals and legumes, but not significantly in fruits and vegetables. Stilbenes have received much attention due to their suggested anti-carcinogenic properties (Figure 5.7). Resveratrol belongs to this group; it accumulates in response to pathogens and other stresses in grapes (Langcake and Pryce, 1976). It has also been identified in other fruits, such as blueberries. Lignin was described above. Due to its very low solubility and digestibility, its contribution to antioxidant activity is negligible.

Relationship between phenolics structure and antioxidant capacity

The structure of phenolic compounds is directly related to their antioxidant properties. Increasing the degree of hydroxylation of the aromatic rings increases the antioxidant activity of hydroxycinnamic acids (Fan et al., 2009). Caffeic acid has more AOX capacity than *p*-coumaric acid. More hydroxyls in the B ring also increases the antioxidant activity of anthocyanins (Cao et al., 1997). Hydroxyls in the *ortho* configuration enhance antioxidant activity (Zheng and Wang, 2003; Kähkönen and Heinonen, 2003). The antioxidant activity of phenolic acids is enhanced by other electron-donating groups associated with the rings (Jing et al., 2012).

Glycosylation has variable effects on the antioxidant capacity of phenolic compounds. Often anthocyanins have similar or slightly less antioxidant activity than the corresponding anthocyanidin. Cyanidin, delphinidin and malvidin have

Table 5.9 Anthocyanidin Concentrations in Common Fruits

Fruit	Content (mg/100 g FW)
Acai	53.6
Acerola	22.6
Apple Fuji	0.7
Apple Gala	1.1
Apple Golden	0
Apple Granny Smith	0
Apple Red Delicious	3.8
Avocado	0.3
Blackberry	90.6
Blueberry	141.0
Cherry	27.7
Cranberry	85.5
Currant black	154.8
Currant red	75.0
Currant white	0
Eldberry	485.3
Grape Concord	65.6
Grape red	44.0
Grape green	0
Kiwifruit	0
Melon	0
Nectarine and peach	1.8
Pear	12.2
Pineapple	0
Plum red	7.0
Plum black	39.7
Plum yellow	0.3
Raspberry	40.9
Strawberry	23.8
Watermelon	0

Adapted from Bhagwat et al. (2011).

similar AOX capacity to their glycosylated derivatives. However, arabinose and rutinoside glycosides have less antioxidant capacity than glycosyl derivatives. The 3,5-diglucosides of cyanidin and malvidin have less AOX activity than the corresponding monoglycosides (Kähkönen and Heinonen, 2003; Zheng and Wang, 2003). Flavonols are usually more potent antioxidants than anthocyanins due to a 2,3 double bond associated with a 4-oxo function. (Zheng and Wang, 2003; Melidou et al., 2005).

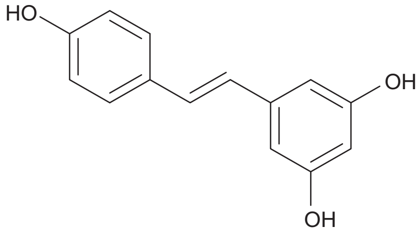

FIGURE 5.7

Structure of resveratrol. This compound has been studied in detail in grapes and may have anti-carcinogenic properties.

F Sulfur antioxidants

Sulfoxides and glucosinolates are among the most important sulfur antioxidants present in vegetables. Sulfoxides are common in vegetables of the genus *Allium*, particularly garlic (*Allium sativum*), one of the oldest medicinal plants. The major sulfur compounds in intact garlic are δ-glutamyl-S-allyl-L-cysteine and S-allyl-L-cysteine sulfoxide (alliin) (Butt et al., 2009). When raw garlic is chopped, the sulfoxides are converted to unstable thiosulfinates like allicin (Lawson et al., 1991). Other thiosulfinates include allylmethyl-, methylallyl- and trans-1-propenyl-thiosulfinate. Glucosinolates are present in plants of the order Brassicales. They have received great attention because their degradation products are powerful anti-carcinogenic compounds. They consist of a β-D-thioglucose group, a sulphonated oxime moiety, and a side chain derived from methionine, an aromatic, or a branched amino acid (Mahn and Reyes, 2012). In broccoli, the most abundant is glucoraphanin (80%) followed by glucobrassicin.

G Factors regulating the concentrations of antioxidants in fruits and vegetables

Several factors influence the accumulation of antioxidants in fruits and vegetables. Changes in composition from harvest to consumption depend on the compound, commodity, cultural practices, postharvest handling, processing and home cooking conditions (Figure 5.8).

Genetic factors

Species

The species determines the prevalence of specific antioxidants. With some exceptions, most fruits accumulate typical antioxidants (Table 5.6). Berries are particularly rich in phenolics (Zheng and Wang, 2003) and vitamin C (Kevers et al., 2007). Total phenolics correlate with total antioxidant capacity and phenolic compounds in these fruits. In ripe blueberries, ascorbic acid contributes only

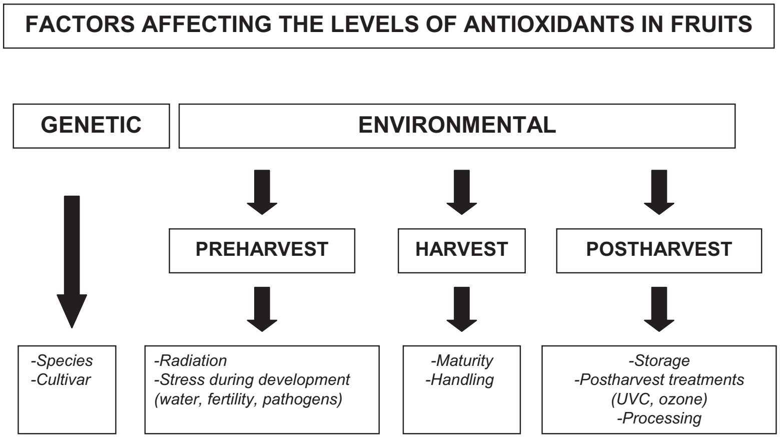

FIGURE 5.8

Factors affecting the concentrations of antioxidants in fruits and vegetables.

0.4–9.0% of total antioxidant capacity (Kalt et al., 1999). The distribution of antioxidants varies among the tissues of a fruit. Water-soluble polyphenolic compounds are found primarily in the skins of peaches, pears and apples. In strawberries, the achenes form only 1% of the total mass but contribute ~11% of the phenolics and 14% of the antioxidant capacity (Aaby et al., 2005). In eggplants, chlorogenic acid is the main antioxidant that accumulates in the inner pulp.

Cultivar

For a given species, antioxidant concentrations vary by cultivar. In six strawberry cultivars, Nelson et al. (1972) found from 19 to 71 mg ascorbic acid/100 g FW. Similar differences among varieties have been reported for phenolics (Wang and Lin, 2000). The identification of lines or mutants that accumulate antioxidants might be useful in breeding programs to improve the nutritional value of fruits and vegetables. Overexpression of high-pigment (*hp*) in tomato increased carotenoid accumulation (Liu et al., 2004). Also in tomato, overexpression of phytoene synthase and lycopene cyclase increased β-carotene and lycopene (Fraser et al., 2002; D'Ambrosio et al., 2004). In carrot, overexpression of β-carotene ketolase from *Haematococcus pluvialis* led to accumulation of the ketocarotenoid astaxanthin (Jayaraj et al., 2007).

Transgenic approaches have increased the concentrations of phenolic compounds. Transformation of tomato with a *Petunia* gene for chalcone isomerase increased the flavonol concentration in the peel by 80-fold (Muir et al., 2001). While the biosynthetic pathway of ascorbic acid is established (Smirnoff, 2000) and most of the genes have been cloned and expressed in various plant species, these strategies have had only limited success.

Environmental factors

Radiation

Modifications in the concentrations of phenolic compounds, ascorbic acid and carotenoids are associated with changes in sunlight exposure. Sun-exposed fruit sides have more phenolics and vitamin C than shaded regions (Lee and Kader, 2000). In leafy vegetables, there are 10 times more flavonols in surface leaves than in internal leaves. Total phenolics doubled in tomato plants exposed to more light. These plants also accumulated more carotenoids and ascorbic acid (Gautier et al., 2008). Thus, radiation interception is important for producing commodities with increased antioxidants. However, the optimal irradiance to maximize accumulation of different antioxidants in fruits and vegetables is not established.

Cultural practices

Several works have analyzed the effect of cultural practices on antioxidants. Strawberries grown with plastic mulch had higher antioxidant capacity than fruits from uncovered beds (Wang et al., 2002). High nitrogen is associated with reduced ascorbic acid (Lee and Kader, 2000). Adding compost as a soil supplement significantly enhanced ascorbic acid (Wang and Lin, 2003). Vitamin C accumulation is inversely correlated with rainfall (Toivonen et al., 1994). Some studies found that organic products accumulated more antioxidants and vitamins than conventionally grown commodities (Woese et al., 1997; Weibel et al., 2000; Asami et al., 2003; Chassy et al., 2006). Other studies found no differences or opposite results (Barrett et al., 2007). A review found that it is not possible to conclude that organically grown products are nutritionally superior to conventional ones (Winter and Davis, 2006).

Maturity at harvest

Fruit developmental stage has a great impact on total antioxidant capacity (Prior et al., 1998) (see also Chapter 15). These changes are highly dependent on the commodity. In tomato and pepper, total antioxidant capacity increases as carotenoids and vitamin C accumulate during ripening. Total anthocyanin increases during ripening in all berries (Wang and Lin, 2000). However, the antioxidant capacity peaks in other species early in development. During blueberry ripening, anthocyanins accumulate while phenolic acids decrease (Rodarte Castrejón et al., 2008). The result is a net reduction of total antioxidant capacity. A similar pattern occurs in strawberry and blackberry (Wang and Lin, 2000). Carotenoids increase during development in pepper, tomato, mango and *Prunus* species (de Azevedo and Rodriguez-Amaya, 2005). In products in which anthocyanins or chlorophylls dominate, carotenoids usually drop during development (Rodriguez-Amaya, 2001).

Wounding

Tissue damage greatly affects total antioxidant concentration. Cell disruption exacerbates the turnover of AsA and phenolic compounds. Eliminating cellular compartmentalization triggers the oxidation of pre-existing phenolics by PPOs and increases hydrogen peroxide, providing the co-substrate for POD-mediated degradation. Wounding also alters phenolic biosynthesis (Tomás-Barberán et al., 1997; Loaiza Velarde et al., 1997). In lettuce, cutting induced phenylalanine ammonia lyase and led to accumulation of chlorogenic acid (Choi et al., 2005). Carotenoid turnover is also accelerated by oxygen, but they are more stable than other AOX groups. Careful handling to minimize physical damage is recommended to reduce antioxidant losses.

Storage

Refrigeration slows the deterioration of vitamin C; in broccoli, losses after seven days storage were 0 at 0°C but 56% at 20°C (see also Chapter 17). Excluding broccoli and banana, most products lose visual quality before significant losses of antioxidant capacity occur (Kevers et al., 2007). Improper temperature management significantly reduces visual quality and thus, consumer acceptance (see also Chapter 13). Ethylene induces accumulation of the bitter iso-coumarin 6-methoxymellein.

Other treatments

Biosynthesis of phenolics is triggered by elicitors like ultraviolet radiation or ozone. In grape, postharvest UV-C and ozone increased accumulation of resveratrol (Cantos et al., 2001; Versari et al., 2001; González-Barrio et al., 2006). Elicitation and accumulation of antioxidant compounds also occurs in other fruits. In blueberry cv. "Bluecrop", reduced UV-C radiation exposure (2 or 4 kJ/m^2) increased the accumulation of anthocyanins and antioxidants (Perkins-Veazie et al., 2008). In strawberry, UV-C also increased phenolic compounds and antioxidants (Ayala-Zavala, et al., 2004). Further studies are needed to determine the feasibility of increasing AOX capacity of fruits and vegetables through manipulation of the postharvest environment (Kalt et al., 1999).

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